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THIS IS UNEVALUATED INFORMATION

1. Since development of military and civil automobile manufacture called for starter batteries which could not be obtained from abroad in sufficient quantities, a starter storage-cell factory was built in the town of Podolsk, 45 kilometers northeast of Moscow, circa 1935 to satisfy this need. Although official yearly production in 1941 was set at 700 thousand units, actual production never exceeded 300 thousand functional batteries due to shortage of raw materials and electric power supply. The factory was a single-story building, but a second floor was added over a part of the main plant, to isolate and house the laboratories and test rooms. Also, an additional lean-to was constructed for the electrical substation, which housed the transformers and rectifiers. Transformers were placed in special concrete chambers with cellars of concrete beneath; in case of fire or explosion, the transformers fell automatically into these cellars, which were then covered by large cement slabs. There were four such transformers; one bank of three, one-phase units for feeding mercury rectifiers, providing DC current for the needs of storage cell production, and one three-phase transformer for light and power. Electric power was obtained from the Moscow government station "Moges"; four mercury rectifiers, with minus six anodes, 50 cycles, 230 volts DC line, and 500 amps were installed in this lean-to, with connecting cables to the substation passed through special channels under the floors of the factory to protect the substation from poisonous fumes.
2. Ventilation was a serious problem, as the sulfuric acid fumes penetrated the entire factory, except for the laboratories, and caused severe health hazards. Actual lead poisoning cases in the factory itself were few, as the doctors readily recognized the early symptoms of same and sent the afflicted person away. Hence, there was a constant turnover of employees; the average span of a worker's employment was five months. Milk, as an antidote, was ordered to be given to the workers, but as it wound up, only government officials visiting the factory received the milk. Ventilation was finally bettered by keeping all of the windows open and having the workers wear heavier clothes.

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3. As far as materials were concerned, very pure lead of good quality from the UK was used (99.996% Pb), as well as Siberian and Fergana--mined lead. Specifications for lead to be used in surface plates, Tudor plates and Plante types were:

Pb	not less than	99.98 %
Fe	" " "	0.002 %
Zn	" " "	0.001 %
Cu	" " "	0.001 %
Sb	" " "	0.005 %
Bi	" " "	0.005 %
Ag	" " "	0.0005%

Unfortunately, the better UK and Soviet leads generally went to the Len Iskra factory in Leningrad. For second-rate production of plates, government specifications allowed lead of "mark C1, OCT/BKC 8032" with specifications as follows:

Pb	not less than	99.93 %
Ag	" " "	0.0015 %
Sb & Sn	" " "	0.0095 %
Bi	" " "	0.05 %
Fe	" " "	0.002 %
As	" " "	0.0015 %
Zn	" " "	0.0015 %

No attention was paid to the quantity of Cu, which was less desirable than Zn. Nothing was said about Mn, quantities of which in Soviet lead were so large that stand-by and floating batteries for electric stations as a rule became dark red when fully charged, due to permanganates formed in the electrolyte.

4. The Podolsk factory often got lead of even poorer quality, but fearing to close the factory because of criticism levied against such inferior materials, kept going in the hope conditions would improve in succeeding shipments. The laboratory was overloaded with experiments upon the "amalgam-ratio" of production, so that often analyses of materials were not performed until after the materials themselves had been used up.
5. Antimony (Sb) was mostly received from abroad, although officially it was supposed to have come from Siberia. Specifications were:

Sb	not less than	99.00 %
Fe, Ni, Cl	" " "	0.05 %
Cu	" " "	0.03 %
Pb	not more than	0.60 %
As	" " "	0.05 %

Grids of Zn, Bi, Cd, Ag, Mn, Sn together, not more than 0.03 %. Neither gold nor Pt could be present in any material even as traces. Laboratory tests showed that one of the chief causes of early failure of storage cells was due to antimony. After 40 or 50 cycles during which antimony appeared to be a very useful addition to the grids of the plates, it began to gather on the minus plates and cause a serious self-discharge, which led to incessant over-charge of the positive plates and its destruction.

6. For this reason, the Podolsk factory started a line of laboratory experiments to determine the optimal minimum of antimony. From 12% of antimony they came down to 7% and then to 2.9%, but then the good mechanical properties fell too much, and poisoning effect upon storage cells remained. Some additions of antimony, to 0.4%, gave better results; antimony was a costly metal which had to be obtained from abroad due to lack of Soviet tin mines of any consequence. Hence was abandoned, but experiments with other alloys [redacted] calcium alloy (0.1% of calcium) with far better mechanical and electrochemical effects. Orders were

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given to the Solikamsk Chemical Factory near the Urals to prepare  $\phi$  lead rich with calcium. This concentrated alloy is added to the lead for grids, and losses of calcium are minimized.

#### 7. Active Mass:

The Podolsk factory used lead oxides for pasting plates; although the Central Accumulator Laboratory (ZAL) made extensive tests in the interest of using lead oxides which produced better cells, only by late 1939 Podolsk began intensifying its experiments in introducing lead powder. Lead oxides were obtained from the Jaroslav Chemical Factory; specifications for both oxides were the same.

Official Specifications				Usual Deliveries	
SiO <sub>2</sub>	-----	0.025	%	0.050	%
Ca	-----	0.0400	%	0.0500	%
Fe	-----	0.0040	%	0.020	%
Zn	-----	0.0010	%	traces	
Cu	-----	0.0010	%	0.010	%
Bi	-----	0.0050	%	0.050	%
Ag	-----	0.0005	%	0.001	%
Sb	-----	0.0050	%	?	
Au / Pt	-----	none		?	
Ni, Co, Mn, Sn, Cd, As -	-----	0.05	%	?	

For some reason, it was felt that those elements listed under question mark in the second column were never present, or that their presence was so unimportant as to eliminate analyses thereon. Oxides were scarce, and frequently materials were accepted without laboratory control.

8. Alloys of many metals were tested, and Ca-Pb was found to be the most suitable. The action of oxide preparation was tested: the subjects of the more specialized tests were the connection between temperature of preparation, humidity content, seeming and real specific density and real specific density, size of particles and longevity of plates. It was found that only greenish or yellow litharge gave longevity to plates, that so-called "double burnt" lead oxide gave poorer results, and oxide with a small content of Pb metal (1.0 - 1.5%) gave a longer life, since its addition for positive plate paste made the plates stronger in handling and negative plates showed a longer life as indicated in the following table:

<u>Type of PbO</u>	<u>% of Pb Metal</u>	<u>Grms In Inch</u>	<u>Absorbing Time of Hardening In Mixer</u>			<u>Life Cycles</u>
PbO, first burning (green-yellow)	1.17%	32	3	0.9	35'	105
	5.9 %	44	5.5	2.64	-	115
Second burning (reddish-brown)	0.90	36	4.17	1.55	1'	45

#### 9. Water:

Water presented a serious problem, for in the Podolsk area it was highly polluted and could not be used. Preparation of large quantities of distilled water was difficult due to a serious shortage of fuel. A project was undertaken to employ the Siemens Electrical Water Purification system, but was abandoned due to the "rooms" inability to supply sufficient electrical power to the factory. Rain and snow water in Podolsk was polluted by factory smoke from Moscow. According to official standards, the following were the water requirements for storage cell production:

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Water for Electrolyte (OST/VKS 2355)

Color	-----	Colorless
Suspension	-----	Traces
Pt	-----	none
Sb & As	-----	none
Mn	-----	0.004 %
Fe	-----	0.00005%
Cu	-----	none
Ag	-----	none
N in any form	-----	0.0008 %
Cl	-----	0.001 %
Organic Substances	-----	0.0001 %

Sometimes it was possible to obtain condensate from the nearby electrical station, a turbine condensate which contained some lubricating oil which was not harmful. The factory laboratory prepared its own distilled water for test uses on a kerosene stove. Tests showed that some impurities were not dangerous for starter cells; Cl is evolved from the cell during its boiling, so that after three to four charges, 0.01% of Cl added to the electrolyte disappeared completely. Damage to the cell was not as much as expected. Mn proved less harmful than Fe, for during the charge, Mn disappeared from the sphere of action, falling to the bottom together with the shedding material as  $MnO_2$ .

10. Sulphuric Acid:

Sulphuric acid was obtained from Soviet chemical factories, and varied greatly in quality. Here are two examples of (a) acid by official standards and (b) acid that was used as a good one but which actually was not:

(a) Sulphuric Acid OST VKS 5355

Specific density (15.5C)	-----	1.835
% $H_2SO_4$	-----	93.19
Color	-----	Colorless
Suspended Matter	-----	none
Pt	-----	traces
As & Sb	-----	"
Mn	-----	"
Fe	-----	0.005 %
Cu	-----	0.0025 %
Cl	-----	0.001 %
Organic Substance	-----	none
Nitrates & Nitrites	-----	none

(b) Test Sample of Sulphuric Acid Obtained:

Specific density	-----	1.80 to 1.84
% $H_2SO_4$	-----	92 to 93.2
Color	--	Often yellow or brown due to packing straw.
Suspended Matter	-----	Frequent Traces
Pt	-----	Usually none
As & Sb	-----	As, traces; Sb, none
Mn	-----	0.0025 to 0.005 %
Fe	-----	0.01 %
Cu	-----	0.005 %
Cl	-----	0.002 %
Organic Substances	-----	Serious traces at times
Nitrates & Nitrites	-----	Traces

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5.

Experiments showed that Cl, N and As disappeared after a few charges with a good boiling of cells. The Len Iskra plant, due to war contracts, was far more careful on the question of impurities.

#### 11. Grids:

For the most part the Podolsk plant copied US types of starter cells, with some changes introduced later. Grids were cast in hand forms; to prevent sticking of grids to forms, the latter were smoked by acetylene-torch flame. By 1939, experiments were underway to simplify grids; part of the horizontal threads were cut away, which lightened the plates and raised their capacity, but resistance of positive plates grew, which was bad for starting motors. No ill effect on the negative plates were noted.

12. As the life of starter batteries was 80 to 90 cycles, the thickness of plates was increased in 1940 from 2 mm to 2.5 mm, and in 1941 plates of 3.5 mm thickness were tried, which actually increased the capacity to 120 cycles, but not 200 cycles as was reported. The percent of stibium (antimony) was reduced from 13% to 6.3%, and orders were given to use Ca alloys; however, World War II interfered, and use of Sb alloys was continued.

13. The Leningrad Metallurgic Factory built an automatic machine for grid-casting which broke down after a trial run and was not used again. Finished grids were sent to storage where they remained for a month in order that all stains might disappear. Lead alloy was prepared in large kettles; temperature of metal could not be over 500°C centigrade, and furnaces were heated by coal.

#### 14. Pasting and Paste:

Pasting was done both by hand and by machine, pasting by hand was slow, but gave better results. Machines resembled German-type machines, [redacted] factory trademarks were replaced with Soviet labels. Oxide paste, [redacted] was made as follows:

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- (a) For plus-minus plate,  $PbO_2$  - 50% and  $PbO$  - 50% were placed in a German-type mixer of 360 liters capacity. After a good 15-minute mixing, the first water equal to 2.5% is added, mixed energetically and then  $H_2SO_4$  - 17% (d = 1.05) is added and mixed for 15 minutes; then the second water equal to 2.5% is added and after five minutes of mixing, water is carefully added by small portions until the necessary pasting thickness is obtained.
- (b) For minus plates,  $PbO$  - 100% and  $H_2O$  - 10% with a 1% expander was used, in the same manner as described in the plus-minus operation.
15. After strong advice to turn to lead powder instead of oxides, the Podolsk factory began to reconstruct its operations. Two types of mills for powder were available:
- (a) A German mill; two bronze cylinders inside a steel one, with a smaller one producing 20 to 30 kg per hour, and a larger one producing 60 to 80 kg per hour, working C = 70 to 90, powder oxidation = 50 to 60% of  $PbO$ .
- (b) A US mill; cylinders were longer, with air and Pb balls fed through the hollow axis, and ready powder taken from the holes at the end of the outer cylinder. Oxidation = 60 to 70%, working C = 135, producing two to three hundred kg per hour.

Following were the characteristics of powders used:

- (a) Graviometric consistency - no grains, and 90% must pass through the sieve of 300 mesh.

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- (b) Volume weight - 39 gram / inch
- (c) Oxidation degree - 50 to 75 %. Powders with the oxidation degree below 50% could be added to the paste of minus plates in quantity equal to 10%. Best oxidation was 50 to 60%. "Burnt" powder could not be used in a pure state, but could be used as a five to 10 % addition to the plus plates:

(d) Seeming Specific Weight	Plate Capacity	Plate Life
1.60 - 1.85	Good	Short
1.85 - 2.15	Good	Long (80 to 100 cycles)
2.15 - 2.40	Poor	Short

16. Then the newest paste, Nr5, was ordered for starter cells, negative plates, consisting of:

- (a) Pb powder - 100 kgs.
- (b)  $H_2SO_4$  - ( $d = 1.40$ ) 180 liters.
- (c) Expander - 35.4 kgs
- (d) Water (in 18 portions) - 69.9 kgs

The above was mixed for two hours and 20 minutes, at a temperature of 70° to 80° centigrade. Paste Nr 5 was especially intended for negative starter plates; lead powder for this paste had to answer the following specifications:

- (a) Color - greyish green
- (b) Absorption number - 13 to 16
- (c) Through a standard (Taylor's) sieve of three hundred mesh at least 50% had to pass, and not more than 25% was allowed to remain on the one hundred mesh sieve.
- (d) Sulfation coefficient - 38 to 40
- (e) Quantity of PbO - 52 to 65%
- (f) Volume by weight - 32 gram / inch

Negative plates made with this paste gave the following trouble; if they were not properly dried, due to the high water content, they then became covered with bubbles which during further processing cracked, and the active mass started peeling off.

17. Powder paste for positive plates: to 500 kgs of well-mixed Pb powder, 18 portions of 2.5 kgs of water were gradually added and agitated. Then 26.5 kgs of water were added and mixed for one hour and 30 minutes, followed by the addition of 45.6 kgs of  $H_2SO_4$  ( $d = 1.32$ ).

18. Expander:

The following was the best expander formula used:

140.5 kgs of water was placed in a mixer, and to it added 162.5 kgs of  $H_2SO_4$  ( $d = 1.83$ ). To this solution (its  $t^{\circ}C = 95$  to 110 degrees centigrade) were added 250 kgs of cotton waste, and mixed until the entire mass became a brownish, glue-like liquid, with no threads apparent. Then 73.2 kgs of  $H_2SO_4$  was added and well mixed. The mixture was cooled to 35 degrees centigrade, and 21.94 kgs of naphtha black added, an oil soot especially

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prepared by burning oil with insufficient air. The expander was then ready for use, with a specific density of 1.5.

19. Starter cells without the expander had a life of 80 cycles; with expander, life expectancy was 180 cycles.  $\text{BaSO}_4$  was an addition that made the expander cheaper; it did not help greatly, and an excess caused swelling and cracking of negatives. The best  $\text{BaSO}_4$  was that prepared by mixing  $\text{Na}_2\text{SO}_4$  and  $\text{BaCl}_2$ , which was expensive, so that heavy Spath from the Bindugi mines was used. Specifications for expander materials:

(a)	$\text{BaSO}_4$	-	99.44 %
(b)	Cl	-	Traces.
(c)	$\text{CaSO}_4$	-	0.73 %
(d)	Fe	-	0.11 %
(e)	$\text{SiO}_2$	-	2.02 %
(f)	Volatile Matter	-	2.89 %
(g)	Heavy metals	-	none
(h)	Volume by weight	-	24.4 gram/inch (Scott)

Specifications for cotton waste:

(a)	$\text{SiO}_2$	-	0.6 %
(b)	$\text{Fe}_2\text{O}_3$	-	1.15 %
(c)	CaO	-	0.4 %
(d)	MgO	-	0.4 %
(e)	Ash	-	2.0 %

Specifications for  $\text{H}_2\text{SO}_4$  for expander:

(a)	$\text{H}_2\text{SO}_4$ monohydrate	-	92 to 93 %
(b)	Color	-	colorless
(c)	Fe	-	less than 0.015 %
(d)	As and Pt	-	absent.

20. The Len Iskra plant in Leningrad used pure storage cell sulphuric acid, chemically prepared  $\text{BaSO}_4$  and good cotton wadding for its expander, with good results. When the Podolsk factory tried to replace naphtha black with filburgine (acetylene soot) results were bad, with great swellings and washing off of active mass already formed on the plates. Prepared expander could be kept no more than 24 hours, it was found, for after that time the process of further carbonization of cellulose as well as changes in  $\text{BaSO}_4$  made it unfit for use.

#### 21. Pasting:

Pasting was done by a pasting machine. On a rubber table, sheets of blotting paper were spread to prevent paste sticking to the rubber. After the plates were pasted, they were covered by sheets of blotting paper and pressed by a rubber roller. In this way the paste was better pressed to the grid, and excess water was pressed out, since plates were not dried after pasting. The process was done in large tanks, for both positive and negative plates together. The Len Iskra factory at Leningrad did their processing in an ammonium electrolyte, and suggested to the Podolsk factory the following formula as giving the best results for positive and negative plates in one tank:

(a)	$(\text{NH}_4)_2\text{SO}_4$	-	100 to 120 kgs
(b)	$\text{H}_2\text{SO}_4$ (d = 1.83)	-	40 to 45 kgs.
(c)	$\text{I}_2\text{O}$	-	1,000 kgs
(d)	J-begin	-	0.25 A/Dec

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- (e) J-middle - 0.18 A/Dec
- (f) J-end - 0.12 A/Dec

The best temperature for both plates was  $\neq$  15 degrees centigrade; lower temperatures resulted in buckling of positive plates during the process.

22. The Podolsk factory, however, preferred its own formula changes as follows:

- (a)  $H_2SO_4$  -  $d = 1.150$
- (b)  $t^\circ C$  = 15 degrees centigrade
- (c) J-begin - (for 70 hours) - 0.18 A/Dec
- (d) J-middle - 0.125 A/Dec (for 80 to 90 hours)

This reduction was to save the positive plates from damage by an extra charge. The higher the current density, the better the efficiency, but weaker the plates. Cementation of plates before formation was found to be useless and even harmful due to cracking of the negative plates when the concentration of acid in electrolyte was allowed to exceed 150 gram/liter.

23. Scaling:

Plates containing gases in the active mass ( $N_2CO_2$ ) formed films of lead sulfate on the surface of plates that did not allow electrolyte to penetrate. Slow dipping of plates into the formation tanks proved a remedy against this. The Len Iskra plant complained that they found strong scaling when the  $(NH_4)_2SO_4$  concentration ran over 150 gram/liter. The presence of alkalies damaged plates. Positive plates suffered especially, and active mass was weaker and the shedding effect stronger. Presence of  $NH_4$  ions acted in the same manner, which is the reason the Podolsk factory did not use ammonia electrolyte. Nor could the factory obtain a good formation effect with positive plates pasted with a pure lead powder. Small additions of  $Pb_3O_4$  were necessary, otherwise the formation lasted a long time, and only 55% of positive plates were formed. Positive plates with pure Pb powder made oxygen from the start, and even a long formation could result in no more than 80% of lead sulfate passed into lead dioxide. Another reason the Podolsk factory rejected the Len Iskra ammonia process was due to the necessity of washing the plates, after formation, first in an acid of  $d = 1.120$  and then twice in distilled water. After formation at Podolsk, plates were rinsed, usually only once, and placed in drying stands. Experiments were underway in 1941 to dry them in a flow of warm air of from 30 to 40 degrees centigrade.

24. Assembly:

Plates were brought into the assembly section, gathered into blocks, and sealed, after which they were sent to automobile factories. These were at first sent unfilled and uncharged, but later it was ordered that they be sent in a slightly formed state, the formation to be completed at their destination.

25. Research at Podolsk:

Many valuable research problems were studied in the Podolsk laboratory, which were never put into practice by 1941 due to government red tape. They worked out a method of block formation which resulted in batteries with a life cycle of 120 to 150, which at that time was considered good in the USSR. Plates were grouped in blocks, and formation done in a weak electrolyte of  $d = 1.150$ . J begin = 0.45 A/D<sub>2</sub>, and after 36 hours a J middle = 0.3 A/D<sub>2</sub> for 40 hours. Then blocks were replaced, sealed, filled with acid of  $d = 1.40$  and charged with J = 0.46 A/D<sub>2</sub>.

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As there was a weaker acid in the pores of plates and separators, concentration of acid fell to 1.280. The charge was made till the voltage of cells came to 2.5 volts. Such an initial treatment brought batteries to within 50% of their official capacity, and increased with every new charge. Town gas with air enriched by oxygen was used for soldering instead of hydrogen.

## 26. Separators:

Wood separators were used exclusively at Podolsk, although due to shortages of lumber, it was ordered that a substitute be found. The Len Iskra plant began using glass separators that did not dissolve in sulphuric acid, in 1941, for military batteries. Wooden separators have a positive side; they give into the electrolyte small quantities of lignin which acts positively upon negative plates, reducing the aging of the negative-active mass. Some of it, however, gets oxidized near the positive plates, and damaging acetic acid is formed. Preparation process was as follows:

- (a) Wood separators were obtained from a nearby plywood factory.
- (b) From storerooms, they were sent to the separator section and loaded into perforated baskets and sunk into tanks filled with five percent solution of NaOH. This solution was kept at  $t^{\circ}\text{C}$  - 40 to 50 degrees centigrade by a barboteur. Separators were soaked for 1-2 hours.
- (c) Then the alkali solution was poured away as quickly as possible and replaced by fresh water, and all the while protected from the action of fresh air as much as possible. Water was heated and mixed with steam; NaOH tars, soaps and all soluble matters washed away. After being washed, separators pass through a lamp-controlled apparatus, consisting of a long rubber belt with a hole in the middle, and defects are rejected.

27. Separators are then put into neutralization tanks with  $\text{H}_2\text{SO}_4$ ,  $d = 1.05$ . After soaking for 24 hours, they are taken out, placed in cold water tanks, and sent to the assembly room. They must be kept either in water or covered with wet clothing. This process is called tepid cleaning; it results in separators that have the same life as batteries. Several ways were proposed: Cold washing, where minus 15 degrees centigrade of NaOH solution was used with 70 to 90 hours of soaking. Separators have a small Ohm resistance; they are sufficiently free of impurities and are mechanically strong, but the process takes much time and floor space. The hot process, which takes eight hours in a 100 degree centigrade solution of NaOH, is a quick, economical process, but results in mechanically weak, short lived separators. Oak was found unsuitable. Redwood was suitable if the hot method was used; with leafy wood, only the cold method was possible.

## 28. Jars:

The most used batteries in the USSR were 3-ST-85, 3-ST-114, and 3-ST-142, meaning three cells in one block, six volts, starter 85, 114 and 142, the ampere hours of each type. Sometimes these cells were marked 3-STP-85, etc., the addition of the letter "P" meant that the block backs were made of plastic. These so-called "plastics" had nothing to do with real plastics, such as vinyls, or polystyrols, but instead were mixtures of Trinidad asphalt, bitums from oil-cracking factories, finely ground wood, cotton waste and asbestos. Various combinations of these materials were used for plastics in starter batteries, which was a source of constant trouble as they sooner or later developed leaks, sometimes within the first month of use. Ebonite jars were good in this sense; they seldom leaked, and could be glued as the leaks were on the outside only. One material in particular, known as "Hwag", was used for block backs. This was a mixture of bakelite "A" asbestos and polystyrol, in small quantities. Its specific weight was 1.1, resistance to distention 70 to 175 kgs/cm<sup>2</sup>, bending 1750 to 560 kgs/cm<sup>2</sup>, crushing 416 kgs/cm<sup>2</sup>,  $C = 0.03$  to 1.3%.

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29. Mastics for Covering Cells:

The last formula used in 1941 was:

- (a) Bitum of naphtha - 83%
- (b) Lubricating oil - 12%
- (c) Oil soot - 5%

Laboratory tests at Podolsk showed that a mixture of Trinidad asphalt, bees-wax, naphtha soot and old rubber made a good cell covering; paraffin was harmful. All materials had to be dry, since water even in small quantities resulted in a foaming of materials during its heating, resulting in fire from spilling over. Mountain wax (osocerite) gave bad results due to a high paraffin content.

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